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**Nonlinear Optical Polymers Derived From
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by

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13. ABSTRACT (Maximum 200 Words) A general approach to the development of multicomponent multifunctional stable NLO materials based on sol-gel reactions has been discussed. We have shown that these second order NLO organic/inorganic composites exhibit excellent room temperature stability of the second order optical nonlinearity. The final structure is an orientationally ordered organic/inorganic network. After an initial decay, excellent long term stability at elevated temperatures, ranged from 100 to 120 °C is observed for a number of different systems. The second order optical nonlinearities are reasonably large for practical device considerations.				
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NONLINEAR OPTICAL POLYMERS DERIVED FROM ORGANIC/INORGANIC COMPOSITES

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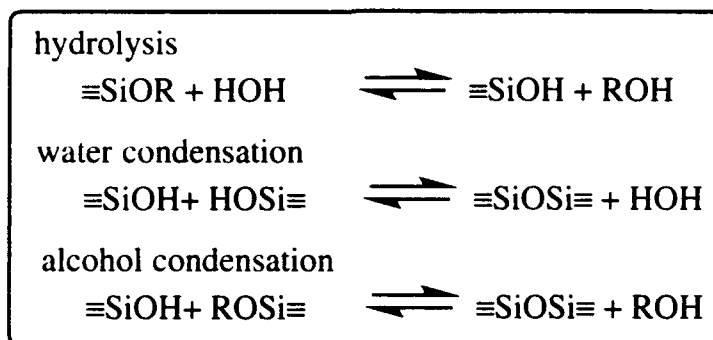
INTRODUCTION

The development of practical materials for second-order nonlinear optical (NLO) applications, such as frequency doubling and electro-optic (EO) modulation, requires simultaneous optimization of their many critical properties. Large second-order optical nonlinearity, its long-term stability at elevated temperatures, and low optical losses are the most desirable features of materials for such types of applications [1,2]. A number of polymeric materials have been reported to surpass both the second harmonic and linear EO coefficients of the traditional inorganic NLO materials such as lithium niobate and potassium dihydrogen phosphate [2].

Second-order NLO properties are present in the polymer when the NLO chromophores are aligned in a noncentrosymmetric manner by the poling technique [3]. In order to prevent the randomization of the poled (aligned) NLO molecules in a polymer matrix, NLO chromophores are usually incorporated into a polymer which has a high glass transition temperature (T_g). This is due to the fact that the molecular motions of NLO chromophores are closely associated with the T_g of the polymer [4]. Further, enhanced temporal stability of second-order NLO properties in a poled polymer can be obtained when a certain degree of crosslinking is introduced [5-10]. Long term stability of second-order nonlinearities in a number of different crosslinked polymeric systems at temperatures higher than 100 °C has been reported earlier [6,9,10].

Sol-gel technology provides an attractive route to the preparation of a three-dimensional inorganic network [11]. In addition, sol-gel materials have been processed to lead to transparent and low loss glasses [12,13]. The basic sol-gel process involves the sequential hydrolysis and polycondensation of silicon alkoxide (Scheme 1) at temperatures that are commonly used to

process polymeric materials [11]. A three-dimensional network of inorganic/organic composites can be prepared by this process without risking the degradation of organic components [14]. By arranging different combination of the starting monomers or polymers, the properties of the multicomponent polymer system (i. e. composites) can be tailored. In light of this, it is feasible that the organic/inorganic composites with the hybrid characteristics of high NLO susceptibility, low optical loss, dense three-dimensional network and high glass transition temperatures, can be achieved.



Scheme 1. The reaction mechanism of the sol-gel process.

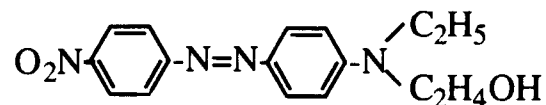
Several types of NLO organic/inorganic composites, which have been developed in our laboratory, provide new angles and methods to the design of second-order NLO materials. They are described as follow.

GUEST ORGANIC CHROMOPHORE / HOST INORGANIC NETWORK

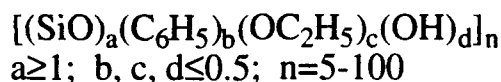
Organic polymeric guest/host systems (NLO dyes as guests and polymers as hosts), which have been studied extensively [2], afford ease of processing and provide a test bed for material characterization. Inorganic matrix based guest/host systems have been developed in our laboratory as well as by others [15-20]. The unique feature of our approach is using a low molecular weight inorganic polymer(oligomer) as a precursor to the network in addition to following the conventional technique using monomers such as tetramethoxysilane and tetraethoxysilane [18-20]. The processability

of the materials is improved by utilizing the oligomer compared to other sol-gel derived systems. Large optical nonlinearity and enhanced temporal stability at elevated temperatures are also observed.

In this approach, a guest NLO dye, Disperse Red 1 (DR1, Figure 1a) was added into a phenyl siloxane oligomer (Figure 1b) solution (Accuglass 204 (A204), available from Allied Signal). The spin-coated guest/host samples were poled and cured simultaneously [15]. This ensures that the NLO dye will be locked in the three-dimensional network. This NLO active guest/host material is named A204/DR1. The design approach in this system is simple and flexible; well established from the development of pure organic guest/host systems. Incorporation of various types of NLO dyes into such sol-gel matrix can be easily achieved. This feature allows fine-tuning of the absorption characteristics of the NLO sol-gel system.



(a)



(b)

Figure 1. Chemical structures of (a) Disperse Red 1 and (b) Accuglass 204.

In order to further enhance the temporal stability of the second order optical nonlinearity, we have developed a general approach to the design of a multifunctional alkoxy silane dye (ASD) [15] which allows NLO chromophores to be covalently bonded to an inorganic matrix. For example, 4-(4'-nitrophenylazo)aniline (Disperse Orange 3) was coupled with (3-glycidyloxypropyl) trimethoxysilane to form an ASD (Figure 2).

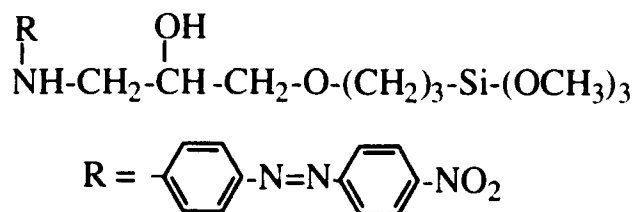


Figure 2. Chemical structure of a Disperse Orange 3 based alkoxy silane dye.

This scheme also allows control of the absorption characteristics by appropriate choice of the NLO chromophore. For example, instead of Disperse Orange 3 as the NLO chromophore in the previous case, 4-nitroaniline can be substituted in order to blue-shift the absorption characteristics. Similar to the preparation of the A204/DR1 mentioned in the previous paragraph, ASD has been incorporated into A204 at high concentrations, where NLO chromophores have been chemically bound to the silicon oxide backbone of the inorganic network after curing (Figure 3). This NLO active sol-gel material is named A204/ASD.

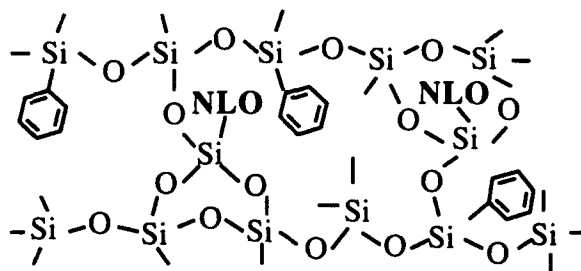


Figure 3. Inorganic network incorporating NLO chromophores.

The poled and cured films exhibit second harmonic coefficients (d_{33}) of 22 and 11 pm/V for A204/DR1 and A204/ASD, respectively. In addition, the second harmonic coefficients (d_{33}) of the poled/cured A204/DR1 and A204/ASD remained unchanged at room temperature for at least 40 h. The temporal stability at 100 °C of second order nonlinearity after poling and crosslinking of A204/DR1 and A204/ASD has been investigated. The results clearly indicate that the stability of poled and cured A204/ASD has significantly been improved. After over 40 h at 100 °C, a reduction of 45%

in d₃₃ was observed for the poled and cured A204/ASD. Most of this loss was in the first few hours of heating. On the other hand, a reduction of 67% in d₃₃ was observed for the poled/cured A204/DR1 after the same thermal treatment. As mentioned earlier, the ASD can be chemically bonded into the cured phenyl siloxane oligomer matrix. The bonding between ASD and the cured siloxane oligomer restricts the molecular motion of the segments and hence prevents the randomization of the ordered NLO molecules.

POLYIMIDE / INORGANIC SYSTEM

In the earlier system, the principle approach was the incorporation of oriented organic dyes into a sol-gel matrix. In this section we report on a scheme that allows the sol-gel reaction to take place in a high T_g polymer matrix. The high T_g of the polymer along with the sol-gel inorganic network would be expected to stabilize the aligned NLO chromophores by decreasing their mobility [16].

Aromatic polyimides have been widely used in the electronics industry because of its low dielectric constant, ease of processing, and high temperature stability [21]. Polyimide films containing a homogeneous dispersion of SiO₂ particles have been achieved by means of a sol-gel process [22]. This type of composite has the characteristics of high temperature processing; high modulus and strength even at high temperatures, and a low thermal expansion coefficient. There are other reasons for choosing polyimide as the polymer matrix in this type of organic/inorganic composite. The internal production of water due to the curing of polyamic acid aids the hydrolysis of the alkoxysilane. Moreover, the carboxylic acid group of the polyamic acid, being a Bronsted acid, might have a catalytic effect on hydrolysis and condensation of the alkoxysilane [23].

Wu et al. have reported on an organic guest/host system where polyimide is used as the host [24]. They have demonstrated that EO response of the poled organic guest/host material is stable at relatively high temperatures (150 °C). We have used polyimide as an organic host and prepared a polyimide/inorganic composite as a second order NLO

material[25]. Alkoxysilane bonded with an NLO chromophore (ASD) (Figure 2) was added to the polyamic acid derived from methylene dianiline and 3,3',4,4'-benzophenonetetracarboxylic acid anhydride (Figure 4). The T_g of the cured undoped polyamic acid (polyimide) is 251 °C. However, the T_g of the cured polyamic acid/ASD (polyimide/ASD) was not observed up to 275 °C, perhaps due to the suppression of the glass transition by the formation of an inorganic matrix network. The onset points of both ϵ' and $\tan\delta$ curves at the α -transition for the polyimide/ASD were found to occur at higher temperatures than that for the undoped polyimide in dynamic mechanical and dielectric analyses [26]. This is due to the fact that the sol-gel reaction of the ASD appears to form a three-dimensional network confinement, which further hinders the translational and rotational motions of the NLO moieties. Following thermal curing and poling, optically clear polyimide films containing NLO moieties were obtained. The poled and cured film of the polyimide/ASD has a d_{33} value of 28 pm/V. The temporal stability of the second order nonlinearity for a poled/cured sample at 120 °C has been investigated. After over 168 hours at 120 °C, a reduction of 27% in d_{33} was observed for the poled polyimide/ASD.

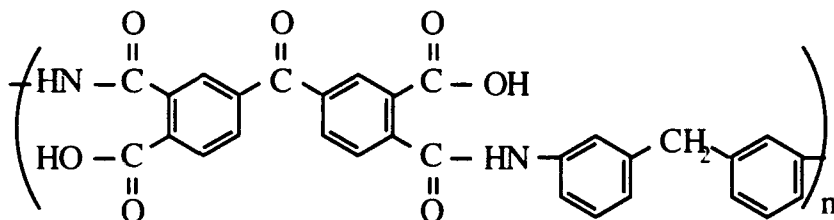


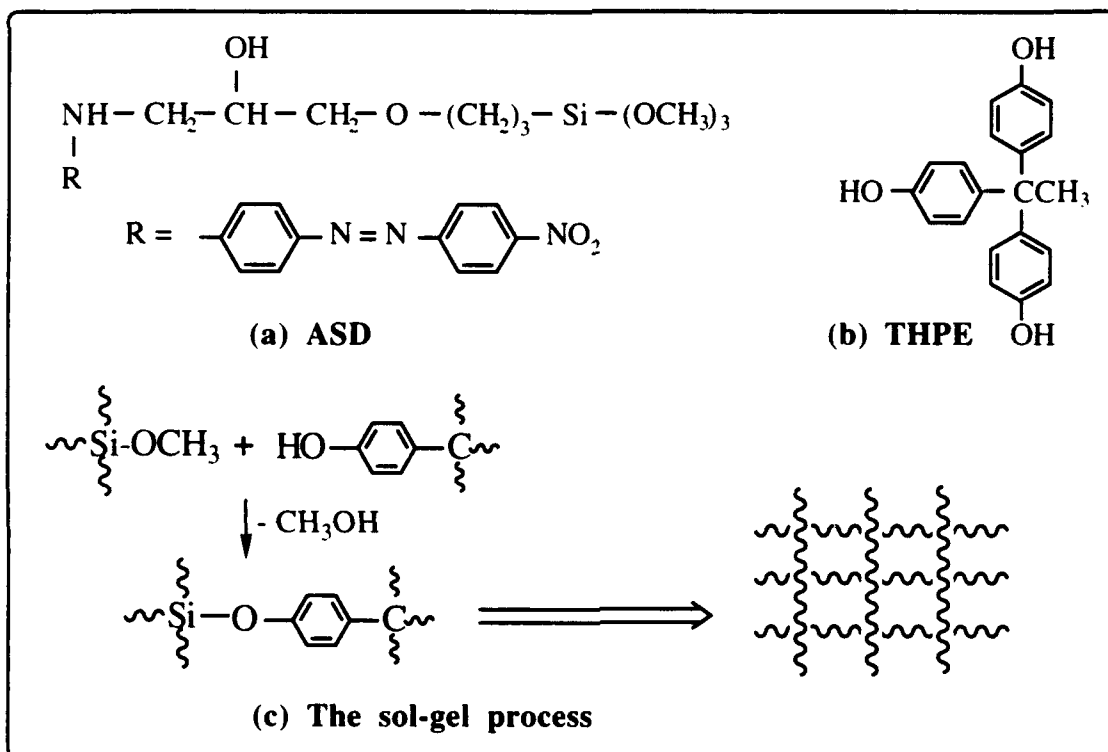
Figure 4. The chemical structure of the aromatic polyamic acid.

This system demonstrated a method to incorporate an NLO inorganic network in a high T_g polyimide matrix. A lower processing temperature and the presence of an inorganic network in this system provide an alternative route for the development of stable NLO materials.

PHENOXYSILICON NETWORK

In this approach, we have extended the sol-gel concept to the polymerization of a multifunctional organic compound and an ASD. Alkoxysilane reacts with aromatic hydroxyl groups to form a phenoxysilicon compound [27], which has been shown to possess excellent thermal stability [28]. In addition, the phenolic compound itself can be designed to be an NLO chromophore, such as (4-nitrophenylazo) resorcinol or 4-nitrocatechol, as well as polymers, such as poly(4-hydroxystyrene) or 2-methyl resorcinol Novolac. The relative size and functionality of the phenolic compound will have a direct bearing on the crosslink density in the cured system.

In one example, a multifunctional molecule, 1,1,1 - tris (4 - hydroxyphenyl) ethane (THPE) and an ASD were mixed together forming a prepolymer through a sol-gel process with the presence of a base catalyst [17]. The spin-coated ASD/THPE samples were cured at 200 °C for 30 minutes. The resulting ASD/THPE sample was found to be amorphous with a T_g of 110 °C. The reaction scheme is shown in Scheme II.



Scheme II. The formation of phenoxysilicon polymer networks.

The poled/cured film has a d_{33} value of 77 pm/V due to its high NLO chromophore concentration (approximately 30% by weight). After being subjected to thermal treatment at 105 °C for 24 h, a reduction of only 19% in the d_{33} value was observed for the poled and cured sample. This d_{33} value remained unchanged under the same thermal treatment for another 144 h. The initial decay of a few percent in the d_{33} value at 105 °C (a temperature close to T_g) is expected. Excellent long term stability is a direct consequence of the extensively crosslinked network [6]. The nonlinear optical coefficient (d_{33}) of the poled/cured sample remained unchanged under ambient condition for at least 168 h.

We have illustrated the preparation of a new class of NLO organosilicon polymers based on a sol-gel process. Aromatic hydroxyl compounds introduced provide the reactive groups for the crosslinking reaction as well as the rigidity of the matrix after curing to further restrict the mobility of the aligned chromophores.

CONCLUSIONS

A general approach to the development of multicomponent multifunctional stable NLO materials based on sol-gel reactions has been discussed. We have shown that these second order NLO organic/inorganic composites exhibit excellent room temperature stability of the second order optical nonlinearity. The final structure is an orientationally ordered organic/inorganic network. After an initial decay, excellent long term stability at elevated temperatures, ranged from 100 to 120 °C is observed for a number of different systems. The second order optical nonlinearities are reasonably large for practical device considerations.

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